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Theory of crystal distortions in $A^{II}B^{IV}C_2{}^{V}$ and $A^{I}B^{III}C_2{}^{VI}$ chalcopyrite semiconductors

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A theory of crystal distortions in ternary chalcopyrite semiconductors is developed, taking into account both covalent and ionic forces. Covalent effects are calculated assuming nearest-neighbor bond-stretching forces, and next-nearest-neighbor bond-bending forces. The effect of the ionic forces is determined by evaluating the Ewald sums for an arbitrary charge transfer between the ions. The observed tetragonal compression and the sublattice displacement in the crystals are found to be primarily due to the covalent forces, and are opposed by the ionic forces. A phenomenological fit to the crystal distortions is also given and discussed.

I. INTRODUCTION

The ternary chalcopyrite semiconductors are of current interest because of their applications in light-emitting diodes[1] and nonlinear optics.[2] Here we investigate the structural properties of the II-IV-V_2 and I-III-VI_2 compounds, and in particular we formulate a theory of the tetragonal distortions and sublattice displacements in these crystals. Our calculations are in agreement with the physical arguments developed by Phillips.[3-5]

We calculate the distortion energy of the crystal in terms of the strains and the sublattice displacements, using the valence-force-field (VFF) model for the lattice dynamics first introduced by Keating,[6] and used by Martin[7] to develop a theory of the elastic constants of the sphalerite compounds. We include the effect of the Coulomb forces on the terms linear in the strains in the distortion energy, but we neglect their effect on the elastic constants, since this gives a small contribution for the binary compounds.[7]

II. COVALENT MODEL

In the following discussion we use $ZnSiP_2$ as an example, and we start with an undistorted chalcopyrite structure, with equal Zn-P and Si-P bond lengths, perfect tetrahedral coordination about the cations, and $x=\frac{1}{4}$ for the sublattice displacement parameter (P coordinate). We use the primitive unit cell with the Zn ion at the origin of the tetrahedral coordinate system, and the lattice constants $a_{0x}=a_{0y}=a_0$, $a_{0z}=2a_0$. The other particles in the unit cell are $\mathrm{Zn}(0,\frac{1}{2},\frac{1}{4})$, $\mathrm{Si}(0,0,\frac{1}{2})$, $\mathrm{Si}(0,\frac{1}{2},\frac{3}{4})$, $\mathrm{P}(x,\frac{1}{4},\frac{1}{8})$, $\mathrm{P}(\bar{x},\frac{3}{4},\frac{1}{8})$, $\mathrm{P}(\frac{3}{4},x,\frac{7}{8})$, $\mathrm{P}(\frac{1}{4},\bar{x},\frac{7}{8})$. The atomic arrangement of the atoms in $ZnSiP_2$ is shown in Fig. 1. The distortion energy for arbitrary strains, $s_{\alpha\alpha}$, where

$$a_\alpha = a_{0\alpha}(1+s_{\alpha\alpha}) \tag{1}$$

and an arbitrary x parameter, where for $\mathrm{P}(x,\frac{1}{4},\frac{1}{8})$

$$x=\tfrac{1}{4}a_0(1+s_{xx}+\eta)\ , \tag{2}$$

where η is the sublattice displacement parameter, can be expanded in powers of scalar invariants,[6]

$$U=U_0+\sum_{klmn} A_{klmn}\lambda_{klmn} + \sum_{\substack{klmn\\pqrs}} B^{pqrs}_{klmn}\lambda_{klmn}\lambda_{pqrs}+\cdots\ , \tag{3}$$

where

$$\lambda_{klmn}=(\vec{x}_{kl}\cdot\vec{x}_{mn}-\vec{X}_{kl}\cdot\vec{X}_{mn})/a_0^2\ , \tag{4}$$

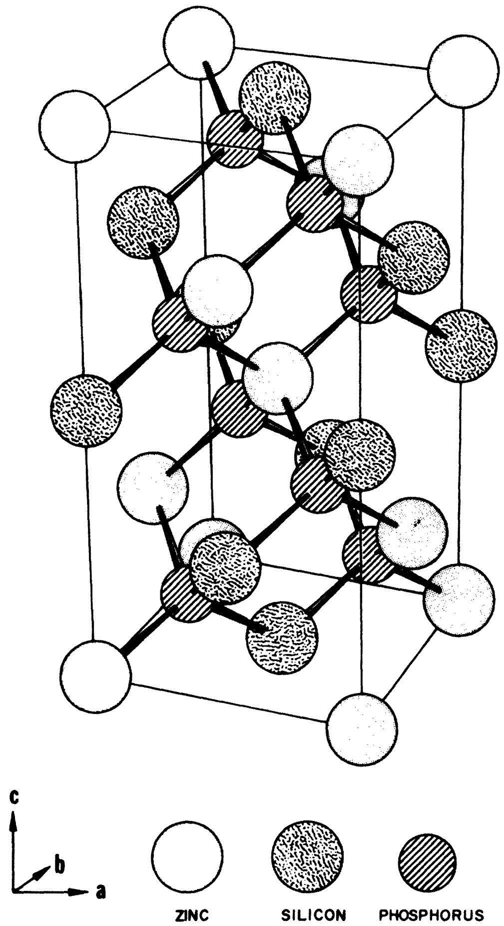

FIG. 1. Atomic arrangement in $ZnSiP_2$.

and $\vec{X}_{kl}=\vec{X}_k-\vec{X}_l$, $\vec{x}_{kl}=\vec{x}_k-\vec{x}_l$, are the separations of the ions before and after the distortion, respectively. The linear term in the expansion does not vanish because the crystal is not initially in the equilibrium configuration. For nearest-neighbor bond-stretching forces and next-nearest-neighbor bond-bending forces there are 14 force constants for the chalcopyrite compounds. For simplicity we assume that the Zn-P-Zn and P-Zn-P bond-bending force constants are equal, and similarly for the Si-P-Si and P-Si-P bond-bending force constants. The ten remaining force constants are divided equally between the linear and quadratic terms in the distortion energy. The linear bond-stretching (bending) constants for the Zn-P and Si-P bonds are denoted by $A_1(A_{11})$, $A_2(A_{22})$, respectively, and $B_1(B_{11})$, $B_2(B_{22})$ are the corresponding quadratic stretching (bending) constants. The linear and quadratic bond-bending constants for the Zn-P-Si bond are denoted by A_{12} and B_{12}, respectively. The notation for the force constants is summarized in Table I.

Substituting Eqs. (1) and (2) in Eqs. (3) and (4) we obtain for the distortion energy per unit cell

$$\begin{aligned}U=&(\delta V/V)^2\left[\tfrac{1}{3}(A'-A'')+\tfrac{1}{9}(A''-A_{12})+\tfrac{1}{12}(3B'+B'')+\tfrac{1}{36}(B_{12}-B'')\right]+\Delta^2\left[\tfrac{1}{6}(A'-A'')+\tfrac{1}{36}(A''-A_{12})\right.\\&\left.+\tfrac{1}{6}B''+\tfrac{5}{72}(B_{12}-B'')\right]+\eta^2\left[(A'+A_{12})+\tfrac{1}{4}(B'+B'')\right]+\epsilon^2\left[\tfrac{1}{2}(A'-A'')+\tfrac{1}{4}(A''-A_{12})+\tfrac{1}{2}B''+\tfrac{1}{8}(B_{12}-B'')\right]\\&+(\delta V/V)\Delta\left[\tfrac{1}{9}(A''-A_{12})+\tfrac{1}{36}(B_{12}-B'')\right]+(\delta V/V)\eta(\tfrac{2}{3}\delta A'+\tfrac{1}{2}\delta B')+\eta\Delta(\tfrac{1}{3}\delta A'+\tfrac{1}{4}\delta B'')+2\eta\delta A'+\tfrac{1}{3}\Delta(A''-A_{12})\\&+(\delta V/V)\left[2(A'-A'')+\tfrac{2}{3}(A''-A_{12})\right],\end{aligned}\tag{5}$$

where

$$\delta V/V=s_{xx}+s_{yy}+s_{zz},$$

$$\Delta=s_{xx}+s_{yy}-2s_{zz}=2-c/a,$$

$$\epsilon=s_{xx}-s_{yy},$$

and

$$A'=\tfrac{1}{2}(A_1+A_2),\qquad \delta A'=\tfrac{1}{2}(A_1-A_2),$$

$$A''=\tfrac{1}{2}(A_{11}+A_{22}),$$

$$B'=\tfrac{1}{2}(B_1+B_2),\qquad \delta B'=\tfrac{1}{2}(B_1-B_2),$$

$$B''=\tfrac{1}{2}(B_{11}+B_{22}),\qquad \delta B''=\tfrac{1}{2}(B_{11}-B_{22}).$$

In deriving Eq. (5) we have put $a_0=1$ for convenience. The magnitude of a_0 can be determined from Eq. (1), using the calculated values of $s_{\alpha\alpha}$, and the observed values of the lattice constants. The force constants $A''-A_{12}$ and $B''-B_{12}$ are nonvanishing if the linear and quadratic bond-bending constants for the Zn-P-Si bond are not equal to the corresponding averages of the Zn-P-Zn and Si-P-Si constants.

TABLE I. Nomenclature for the force constants of the linear and quadratic terms in the distortion energy for the valence-force-field model.

Bond	Linear	Quadratic
A-C	A_1	B_1
B-C	A_2	B_2
A-C-A	A_{11}	B_{11}
C-A-C	A_{11}	B_{11}
B-C-B	A_{22}	B_{22}
C-B-C	A_{22}	B_{22}
A-C-B	A_{12}	B_{12}

We now neglect the terms linear and quadratic in $\delta V/V$ in the distortion energy, on the basis that there is little difference between the volume of a ternary chalcopyrite crystal and its binary analog. We also neglect the difference $B_{12}-B''$ as well as the effect of the linear force constants on the elastic constants. The quadratic terms which stabilize the distortion may then be evaluated using Martin's theory[7] for the binary compounds, and Levine's calculation[2] of the bond ionicities in the ternaries. The distortion energy is now given by

$$U=a_1\eta+a_2\Delta+b\eta\Delta+\tfrac{1}{2}c_1\eta^2+\tfrac{1}{2}c_2\Delta^2,\tag{6}$$

where $a_1=2\delta A'$, $a_2=\frac{1}{3}(A''-A_{12})$, $b=\frac{1}{3}\delta A'+\frac{1}{4}\delta B''$, $c_1=\frac{1}{2}(B'+B'')$, $c_2=\frac{1}{3}B''$. From Eq. (6) we see that, for positive η, the term $a_1\eta$ gives a negative contribution to the distortion energy when $A_1-A_2<0$. Since the Si-P bond is more covalent than the Zn-P bond we expect that $A_2>A_1$, similar to the quadratic bond-stretching constants, for which $B_2>B_1$. Similarly the tetragonal compression lowers the energy when $a_2<0$, which requires that the linear bond-bending constant for the Zn-P-Si linkage must be greater than the average of the corresponding constants for the Zn-P-Zn and Si-P-Si linkages. As pointed out by Phillips,[5] this situation can arise from a deficiency of bonding electrons in the Zn-P-Zn linkage, and an excess of bonding electrons in the Si-P-Si linkage, as compared to the Zn-P-Si linkage.

Minimizing the distortion energy, Eq. (6), with respect to η and Δ gives

$$\begin{aligned}\eta&=(a_2b-a_1c_2)/(c_1c_2-b^2),\\ \Delta&=(a_1b-a_2c_1)/(c_1c_2-b^2).\end{aligned}\tag{7}$$

It is known experimentally[8-11] that to a good approximation the x parameter can be calculated assuming perfect tetrahedral coordination about the B cation, giving

$$x = a[0.5 - (c^2/32a^2 - \tfrac{1}{16})^{1/2}] . \tag{8}$$

Substituting Eqs. (1) and (2) in Eq. (8) we find, to lowest order in the distortion, the relation $\eta = \Delta$. Noting that $B' \gg B''$,[7] and neglecting higher-order terms in the distortion, we get from Eq. (7)

$$a_1/a_2 \simeq \tfrac{3}{2}(B_1 + B_2)/(B_{11} + B_{22}) . \tag{9}$$

The only other restriction on the linear force constants is that they must vanish individually for a binary compound. No relationship between these constants and the ionicities of the bonds and the bond lengths has been found, and we fit the experimental values of Δ to the following expression involving the electronegativities X and the rationalized tetrahedral radii R,[12]

$$\Delta = \alpha R_A^{\beta} R_C^{\gamma} (X_A - X_B)^2 . \tag{10}$$

The form of Eq. (10) is suggested by the approximately linear relationship of the square of the electronegativity difference of the cations with the tetragonal distortion (Fig. 2). The form of the coefficient is chosen to represent the difference in the size of the A and B atoms. A least-squares fit of Eq. (10) for ten II-IV-V_2 compounds gives $\alpha = 0.089$, $\beta = 5.385$, and $\gamma = -1.323$; where R_A, R_c are in Å, and the Phillips electronegativity scale is used.[4,5] The calculated values of Δ for the II-IV-V_2 compounds are given in Table II. The agreement with experiment is better than 20%, and in most cases better than 10%. For the I-III-VI_2 compounds there are irregularities which may be due either to the short-range bonding with the d electrons,[3,14] or to Coulomb forces, or both. The effect of the Coulomb forces is estimated in Sec. III. A least-squares fit of Eq. (10) to fifteen I-III-VI_2 compounds gives $\alpha = 0.105$, $\beta = 7.459$, and $\gamma = -3.115$, and the calculated values are given in Table III. The agreement with experiment is better than 20%, although there is on the average a larger deviation than for the II-IV-V_2 compounds. A fit of Eq. (10) for both the II-IV-V_2 and I-III-VI_2 compounds with a single set of parameters gives poor agreement with experiment, with errors as large as 50%.

Expressions for the force constants a_1 and a_2 can be obtained from Eqs. (7), (9), and (10). The most promising approach for determining the unknown force constants however is to calculate the ir and Raman spectra for the ternary chalcopyrite crystals. Measurements[15-18] for a number of compounds show a more complicated spectrum than for a typical zinc-blende crystal, and the splitting of the extra lines can be related to the unknown force constants and the crystal distortion. A more complete theory along these lines is required to explain the accurate measurements of the x parameter carried out by Abrahams and Bernstein[8-11] for a number of the II-IV-V_2 and I-III-VI_2 compounds.

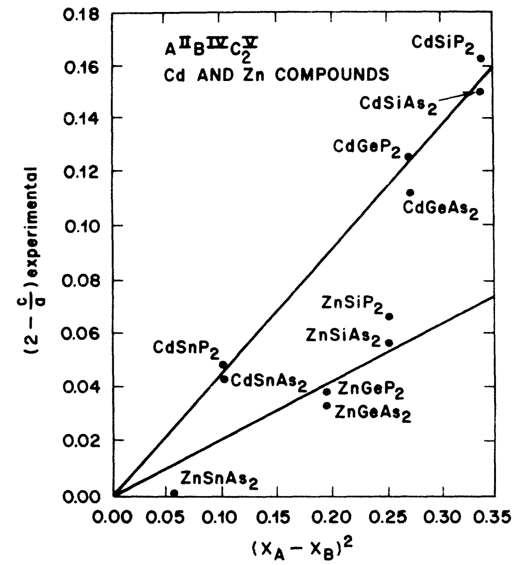

FIG. 2. Diagram showing linear relation between Δ_{expt} and $(X_A - X_B)^2$ for II-IV-V_2 compounds. The solid lines are drawn for reference only.

We make a final comment about the form of the expression, Eq. (10). The correlation of Δ with $(X_A - X_B)^2$ is an experimental fact, and it is tempting to regard Eq. (10) as part of an expansion of the form

$$\Delta = \alpha_1 (X_A - X_B) + \alpha_2 (X_A - X_B)^2 + \dots . \tag{11}$$

It can be argued that the odd terms in the expansion should vanish because the crystal is invariant under interchange of all the A and B atoms, and hence has the same Δ. The expansion parameter moreover is small, and there should be no problems with the convergence of the series. We would like to point out that such an interpretation of Eq. (10) may be incorrect. Although the crystal distortion is relatively small, on a microscopic level there may be considerable charge redistribution as compared to a zinc-blende type of binary compound, and an expansion of Δ as a power series in $(X_A - X_B)$ may not exist. Furthermore, it is not clear whether such an expansion should be carried out starting from the binary analog of the ternary compound, or some other starting point. If Eq. (10) is part of a series expansion in $(X_A - X_B)$, then the coefficient of $(X_A - X_B)^2$ should be evaluated for $X_A = X_B = X_0$ and should be a symmetric function in A and B. A symmetric function does not

TABLE II. Experimental and calculated values of the tetragonal distortion $\Delta = 2 - c/a$ for the $A^{II}B^{IV}C_2^{V}$ compounds. The calculated values are based on Eq. (10) with $\alpha = 0.089$, $\beta = 5.385$, and $\gamma = -1.323$. The experimental values are taken from Ref. 13, except in the case of $ZnSiP_2$ (Ref. 8), $CdSiP_2$ (Ref. 9), and $CdGeAs_2$ (Ref. 11).

	Δ_{expt}	Δ_{calc}
$CdSiP_2$	0.164	0.159
$CdSiAs_2$	0.151	0.143
$CdGeP_2$	0.123	0.128
$CdGeAs_2$	0.113	0.115
$CdSnP_2$	0.048	0.049
$CdSnAs_2$	0.044	0.044
$ZnSiP_2$	0.067	0.057
$ZnSiAs_2$	0.057	0.051
$ZnGeP_2$	0.039	0.044
$ZnGeAs_2$	0.034	0.039

fit the experimental data, however. Hence the correlation between Δ and $(X_A - X_B)^2$ is not understood.

III. IONIC MODEL

In this section we estimate the amount of tetragonal distortion caused by charge transfer from the A cation to the B and C ions. In order to obtain a quantitative estimate, we assume that the terms linear in the distortion are due only to the Coulomb forces, and that the restoring forces are determined by the elastic constants. We neglect the sublattice displacement, since the piezoelectric strain constants for these compounds have not been measured and it is not known how strongly the ionic forces couple the sublattice displacement to the tetragonal strain. It can be seen qualitatively, however, by considering the interaction for second neighbors, that the Coulomb forces favor a tetragonal dilatation of the crystal, instead of a tetragonal compression as caused by the covalent forces. Furthermore the sublattice displacement is in the opposite sense to that in the covalent model. This can been seen from a tetrahedron with a C ion at the center. If there is a charge transfer from the A ions to the B and C ions, the Coulomb force on the C ion is towards the A ions, which is opposite the direction for the covalent force. Hence the tetragonal strain and the sublattice displacement due to the Coulomb forces are coupled and opposite to the distortions caused by the covalent forces. The fact that the II-IV-V_2 compounds and most of the I-III-VI_2 compounds show a tetragonal compression rather than a dilatation is evidence for the weakness of the polar binding in these crystals.

We assume that the charges on the A, B, and C ions are e_1, e_2, e_3, respectively, and we must have $e_1 + e_2 + 2e_3 = 0$ for charge neutrality of the unit cell. We follow the treatment of Keffer and Portis,[19] who have carried out a similar calculation for the wurtzite-type compounds. The energy density of the crystal, U, is expanded in powers of the strains, $s_{\alpha\beta}$, about the equilibrium crystal configuration, which in this case is the ideal zincblende structure,

$$U = U_0 + \sum_{\alpha\beta} \left(\frac{\partial U}{\partial s_{\alpha\beta}}\right)_0 s_{\alpha\beta} + \frac{1}{2} \sum_{\substack{\alpha\beta \\ \alpha'\beta'}} \left(\frac{\partial^2 U}{\partial s_{\alpha\beta}\partial s_{\alpha'\beta'}}\right)_0 s_{\alpha\beta} s_{\alpha'\beta'} + \dots \quad (12)$$

As discussed before, we assume that the terms linear in $s_{\alpha\beta}$ are due only to the Coulomb forces. Minimizing the energy density with respect to $s_{\alpha\beta}$, we get for the tetragonal strain

$$\Delta = 2 \sum_{\beta} (d_{z\beta} - d_{x\beta}) \left(\frac{\partial U}{\partial s_{\beta\beta}}\right)_0 , \quad (13)$$

where d_{ij} is an element of the compliance matrix. In the absence of information about the elastic constants, we assume $d_{xx} = d_{zz}$, $d_{xy} = d_{xz} = d_{zx} = d_{yz} = d_{zy}$, and Eq. (13) simplifies to

$$\Delta = 2(C_{11} - C_{12})^{-1} \left[\left(\frac{\partial U}{\partial s_{zz}}\right)_0 - \left(\frac{\partial U}{\partial s_{xx}}\right)_0 \right], \quad (14)$$

where $C_{\alpha\beta}$ are the elastic constants. The evaluation of the derivatives of the energy density and the resulting Ewald sums for the ideal chalcopyrite structure is a straightforward but lengthy procedure, and we give the result

$$\Delta = -0.437 \frac{(e_1 - e_2)^2}{a^4(C_{11} - C_{12})} . \quad (15)$$

TABLE III. Experimental and calculated values of the tetragonal distortion $\Delta = 2 - c/a$ for the $A^{I}B^{III}C_2^{VI}$ compounds. The calculated values are based on Eq. (10) with $\alpha = 0.105$, $\beta = 7.459$, and $\gamma = -3.115$. The experimental values are taken from Ref. 10.

	Δ_{expt}	Δ_{calc}
$AgAlS_2$	0.199	0.238
$AgAlSe_2$	0.195	0.183
$AgAlTe_2$	0.122	0.120
$AgGaS_2$	0.210	0.193
$AgGaSe_2$	0.183	0.149
$AgGaTe_2$	0.102	0.097
$AgInS_2$	0.080	0.094
$AgInSe_2$	0.077	0.072
$AgInTe_2$	0.040	0.047
$CuAlS_2$	0.042	0.050
$CuAlSe_2$	0.041	0.039
$CuAlTe_2$	0.025	0.025
$CuGaS_2$	0.041	0.038
$CuGaSe_2$	0.034	0.029
$CuGaTe_2$	0.017	0.017

We refer to the paper of Keffer and Portis[19] for more details. The above result gives a negative value of the tetragonal strain, which is to be expected, and it vanishes for a zinc-blende crystal, since $e_1 = e_2$ in this case. As we discussed earlier, we estimate the elastic constant by using Martin's theory[7] for the binary compounds, and Levine's calculation[2] of the bond ionicities in the ternaries. Assuming that $(e_1 - e_2)^2 = e^2$, and using the observed lattice constant we get for $CdSiP_2$ a dilatation which is about 20% of the observed compression. For all of the II-IV-V_2 compounds, and for most of the I-III-VI_2 compounds, we find that the crystal distortion is not predominantly due to polar forces. For $CuInS_2$, $CuInSe_2$, and $CuInTe_2$, all of which have a negative Δ,[11,18] it is not known whether the change of sign of the distortion is due to the Coulomb forces, or to bonding with the d electrons.

IV. CONCLUSIONS

We have shown, using the valence-force-field model, that the tetragonal compression and the sublattice displacement of a ternary chalcopyrite crystal can be attributed mainly to the covalent forces. The distortion occurs because of an excess and deficiency of bond charge in the B-C and A-C bonds, respectively. This results in a shortening of the B-C bond, compared to the A-C bond, with a corresponding shift of the C ion (sublattice displacement). The B-C tetrahedron is consequently stiffer and shows little distortion, while the A-C tetrahedron is considerably distorted. The bond charge distribution also results in the tetragonal compression because the A-C-B bond-bending force constant is not equal to the average of the corresponding A-C-A and B-C-B force constants, and the bond-bending energy is lowered by the compression.

The effect of the ionic forces has been calculated assuming arbitrary charge transfer between the ions, consistent with over-all charge neutrality. The calculated distortion is opposite to that observed for most of the compounds, and is proportional to the square of the difference of the charges on the A and B cations. The ionic effect is of secondary importance for these compounds, with the possible exception of $CuInS_2$, $CuInSe_2$, and $CuInTe_2$, which have a negative $\Delta = 2 - c/a$. It is possible that ionic forces are responsible for this reversal of sign, since the Cu compounds were found to have the largest degree of ionicity of the sphalerite crystals.[7] Before this can be determined, however, it is necessary to know the effect of the shortrange bonding of the d-electrons.

The main difficulty with the present theory is the large number of unknown force constants. This can be resolved by a calculation of the ir and Raman spectra, and by measurements of the elastic constants and the piezoelectric strain constants.

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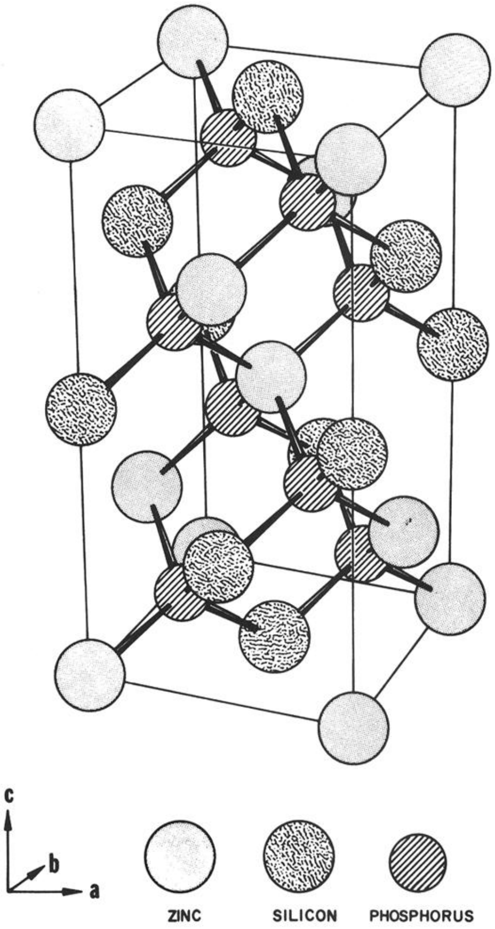

FIG. 1. Atomic arrangement in $ZnSiP_2$.